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THE LABORATORY PREPARATION OF HMX
BY CONTINUOUS NITRATION

21 NOVEMBER 1955

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Written by: B. W. Cross
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Robert Robbins

THE LABORATORY PREPARATION OF HMX
BY CONTINUOUS NITRATION

by

B. W. Cross and E. D. Cochran

ABSTRACT

HMX has been successfully prepared in the laboratory by the continuous nitration of hexamine in two stages. The nitration equipment consists of a cascading series of jacketed nitrators and age pots equipped with Teflon scrapers. The scrapers are necessary to remove the material which is deposited on the cooling surfaces of the vessels. The first stage of nitration can also be effected in a "jeep" which utilizes concentric cooling "legs" similar to those of the RDX nitrators at Holston.

The recommended conditions are essentially those currently employed in the pilot plant batch process at Holston. The resulting purity of the crude product is approximately 87% HMX, the remainder being RDX. The yield approximates 1.5 pounds of HMX on a pure basis per pound of hexamine, which is 71% of theory.

The beta polymorph of HMX can be produced in the nitration step by relatively high usages of acetic anhydride, nitric acid, and ammonium nitrate. Under the conditions studied the product purity and yield are too low to make the direct production of beta-HMX economically desirable.

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I. INTRODUCTION

Continued interest in applications of HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane) as a military explosive led to further studies of the synthesis of HMX. The purpose of this work was twofold:

1. The design of laboratory equipment for preparing HMX by a continuous process;

2. The study of process variables which affect yield, purity, and equipment design.

The ultimate purposes of a continuous process are to reduce the high capital and production costs of HMX, and to attain a minimum explosives load in production equipment.

At the present time HMX is produced at Holston in pilot plant equipment utilizing the batch process for nitrating hexamine in two stages. Development of the laboratory batch process has been reported previously.[1,3,4] In light of subsequent laboratory studies and pilot plant experience, the chemical usages were modified in the evolution of the present pilot plant process. The basic steps of the pilot production process are: a two-stage nitration with two age periods, dilution with water and simmering, filtration and washing, crystallization from acetone, purification by acetone extraction of the bulk of the RDX, and filtration of the finished product.

Development of the continuous nitration process for HMX is based on the adaptation of the batch processes employed in the laboratory and pilot plant. Acetic anhydride and solutions of hexamine-acetic acid and nitric acid-ammonium nitrate are fed into the first nitrator

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which overflows to the first age pot. The effluent and additional amounts of acetic anhydride and nitric acid-ammonium nitrate solution are fed into the second nitrator. The overflow stream is then aged batchwise for 60 minutes prior to simmering and washing the crude product.

In the initial runs of this investigation, the reactants were fed semi-continuously into equipment which was available in the laboratory. The results were encouraging in spite of low yields and rapid coating by HMX of the heat transfer surfaces of the second nitrator. The experience gained aided in the design of laboratory equipment more nearly suited for this experimentation. The equipment was sized for the continuous production of approximately three pounds of HMX per hour. A low speed Teflon scraper was successfully utilized in the second nitrator to prevent coating of cooling surfaces. Later experience from a 110-hour continuous run dictated the use of Teflon scrapers in the first nitrator and the first age pot.

Attempts to use concentric glass heat exchangers in the second nitrator were not successful. However, the exchangers were judged satisfactory when used in the first nitrator. The design simulates that used in plant scale RDX nitrators at Holston. Its high ratio of heat transfer area to working volume permits lower explosive load limits. A nitrator of this design is commonly called a "jeep".

The more significant process variables were investigated so that optimum conditions would be approached in the final design. In evaluating a given set of conditions the following factors were considered: the yield of pure HMX per unit of hexamine, the purity and the filter-

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ability of the crude product, and the tendency toward excessive coating of cooling surfaces.

In the present pilot plant process the filtration and washing of the crude HMX is a critical problem in terms of unit capacity, capital investment, and operating labor costs. The pilot plant application of preliminary crystallization of HMX from acetone prior to washing[2] was unsuccessful in achieving good filterability. This crystallization had the extreme disadvantage of causing some polymerization of acetone. Therefore, the filtration characteristics of the crude product are very important to any proposed process.

Currently the purity of the HMX finished product must be at least 90 percent. Some users require 95 or even 98 percent purity. To obtain these purities, crude HMX is extracted with acetone to remove the required amount of RDX. Due to the solubility properties, approximately one pound of HMX is extracted with each three pounds of RDX. Obviously then, the purity of the crude product will affect the yield and cost of the finished goods.

HMX has an even greater tendency than RDX to coat nitrator cooling surfaces. As compared to metals, glass minimizes the coating but does not eliminate it. The amount of coating affects the cooling capacity and, consequently, the production capacity of a nitration unit. In spite of such design measures as a Teflon scraper, excessive coating is a potential cause for shut-downs in plant equipment. For example, excessive coating of the metal components of the scraper assembly, agitator, and effluent piping would make manual removal of the coating extremely difficult.

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Heat loads and heat transfer performance data were determined for use in future design work.

These studies indicate that HMX can be successfully prepared by the continuous nitration of hexamine to produce approximately 1.5 pounds of pure HMX per pound of hexamine. The composition of the crude product approximates 87% HMX and 13% RDX. The attained pure yield is 71% of the theoretical 2.11 pounds HMX per pound of hexamine.

II. EXPERIMENTAL

A. Apparatus

The equipment used in this project is listed below. A flow sheet (Figure 1) is included in the Appendix.

1. Reactant Feed Systems

   a. Semi-continuous Feeds - The reactants were fed from glass burettes sized for 15 to 30 minutes usage and calibrated for the desired increments to be fed each 15 seconds.

   b. Continuous Feeds - The reactants flowed by gravity from large glass bottles through 1/8" i.d. stainless steel tubing and rotameters to the desired nitrator. Needle type valves were used to regulate the flow rates. The feed tubing was shaped into coils and immersed in an agitated constant temperature water bath preceding the rotameters.

2. Nitration Vessels

   Four different groups of nitrators and age pots were used.

   a. Semi-continuous Design (see Plate 1)

      (1) First Nitrator - An open, cylindrical, agitated, jacketed vessel, 4" diameter x 7" high, with a 4" x 6" vertical baffle.

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For details see "drying pot" described in Ref. 5.

(2) First Age Pot - Similar to above nitrator but 8" high; described as "decant pot" in Ref. 5.

(3) Second Nitrator - Similar to above except for being un-baffled and 4" high. The "mix pot"[5] with a stainless steel propeller type agitator was used.

b. Continuous Design I (see Plate 2)

(1) First Nitrator - A jacketed, agitated vessel, 6" diameter x 4.5" high, with a variable speed propeller type agitator used at 350 to 400 rpm., constructed of type 316 stainless steel. See Figure 2.

(2) First Age Pot - Identical to preceding nitrator.

(3) Second Nitrator - A jacketed, agitated pot, 4" diameter x 4" high, with a variable speed propeller type agitator used at 300-400 rpm. A Teflon scraper, 1/16" thick, was mounted on a supporting assembly which rotated at 10 to 15 rpm. The material of construction of the metallic components was type 316 stainless steel. See Figure 3. A short thermometer of narrow range was mounted on the scraper supporting arms.

c. Continuous Design II (see Plate 3)

(1) First Nitrator and First Age Pot - Similar to preceeding second nitrator except larger, 6" diameter x 6" high. See Figure 4.

(2) Second Nitrator - The second nitrator of Design I de-scribed in Section b (3) was used.

      d. Continuous Design III (see Plate 4)

        (1) First Nitrator - The existing laboratory jeep was used. See Figure 5. The turbo-agitator is designed to circulate slurry through jacketed glass tubes (cooling leg) and was operated at 300-400 rpm. The baffle at the effluent down-spout was adjusted to give a working volume of approximately 2800 ml.

        (2) First Age Pot and Second Nitrator - The vessels described in Design II (Section 2-c) were used.

3. Collection Pot - A closed, cylindrical, agitated, bottom-jacketed vessel, 10" diameter x 12" high. Agitator speed was 250 to 350 rpm. For details see "nitrator" in Ref. 1.

4. Slurry Pump - A model T-6 Sigmamotor pump, variable speed, used with Tygon tubing 1/2" i.d. x 1/16" wall thickness.

5. Final Age and Simmer Pots - Four pots were used which were identical to the collection pot described in Section 3.

6. Motors - A 1/2 hp. Gast air motor was used to drive the agitator of the jeep. All other drive motors were 1/9 hp. Dumore electric motors, Model KLA, which were controlled by Powerstats.

B. Materials

    The chemicals used met the specifications below.

Chemicals	Specifications
1. Acetic acid	99.7% minimum assay
2. Hexamine	99.5% minimum assay
3. Hexamine-acetic acid solution (used as is or added to acetic acid to obtain the desired composition)	62.0 ± 0.3% HOAc

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Chemicals (Contd)	Specifications (Contd)
4. Nitric acid	98.5% minimum assay
5. Nitric acid-ammonium nitrate solution	$56.4 \pm 0.5\%$ HNO_3 $51.7 \pm 0.5\%$ HNO_3
6. Ammonium nitrate (added to 56.4% HNO_3 solution to obtain 51.7% HNO_3 solution)	Merck reagent grade
7. Acetic anhydride	97.5% minimum assay
8. Paraformaldehyde (Heyden)	USP X Grade

C. Experimental Procedure

1. General Procedure for Semi-Continuous Process

The first runs were made using the equipment described in Section
II-A-2-a. The reactants were admitted semi-continuously into the
nitrators.

All equipment is cleaned, dried, and readied for operation. A
heel is placed in the first nitrator consisting of: 300 ml. acetic
acid, 20 ml. acetic anhydride, and 4 g. paraformaldehyde. The
temperature of the heel is adjusted to $44 \pm 1^{\circ}C$. as is the temperature
of the reaction mixture throughout the run. An increment of each of
the three reactants is admitted from the burettes at 15-second inter-
vals in the following order: hexamine-acetic acid, nitric acid-
ammonium nitrate, and acetic anhydride.

The reaction mixture overflows from the first nitrator into the
first age pot, thence to the second nitrator, finally to the col-
lection pot. When the effluent reaches the agitator in each vessel
the agitator is started. The temperature of these vessels is main-
tained at $44 \pm 1^{\circ}C$. throughout the run. When the agitator of the

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second nitrator is started the addition of second-stage reactants is begun, an increment of each feed being added at 15-second intervals in the following order: nitric acid-ammonium nitrate then acetic anhydride.

Collection of a batch in the collection pot and subsequent operations is effected in batch-wise fashion. Pumping of a batch to one of the final age and simmer pots is started in sufficient time to complete the transfer at the desired time. Solid material on the sides and bottom of the collection pot is removed reasonably well with a small amount of acetic acid from a wash bottle. Pumping and rinsing requires about six minutes.

In the final age and simmer pots, the nitration slurry is aged for one hour at $44 \pm 1^{\circ}C$. Then 1300 ml. of water is added and the mixture heated at $98^{\circ}C$. for 30 minutes. The batch is cooled to $30^{\circ}C$., filtered, and washed well with water on two 10" Büchner funnels, dried, and weighed. The product is analyzed by the spectrophotometric method[6] and examined microscopically.

The last batch of each run was usually aged and simmered in the collection pot.

Three runs were attempted which utilized the jeep as the second nitrator. The effluent from the first age pot was pumped to the jeep by the Sigmamotor pump. The baffle in the jeep was adjusted to give a working volume of about 2,000 ml. A heel in the jeep was necessary. The heel was varied from 1,020 ml. to 1,760 ml. of acetic acid containing 2 to 3% acetic anhydride.

2. General Procedure for Continuous Process

The essential differences of the continuous process from the semi-continuous procedure are in the feed system which is described in Section II-A-1-b and the nitration vessels described under b, c, and d of Section II-A-2. Rotameters are used to meter continuously each chemical or solution. The constant temperature water bath in the feed system is operated at $40^{\circ}C$. When used, the Teflon scraper is started just before material enters a vessel.

When paraformaldehyde was fed during a run, it was fed incrementally, e.g., 4 g. each 30 minutes. In most runs, the equipment was operated at a reduced production rate because of materials handling problems.

In the majority of runs using 9.0 g. acetic acid per g. hexamine, the hexamine solution containing 62% acetic acid was diluted with appropriate quantities of acetic acid and the resulting solution (90% acetic acid) then fed to the first nitrator. In five runs, the glacial acetic acid was fed as a separate stream to supplement the 62% acetic acid in the hexamine solution and increase the acetic acid to hexamine ratio to 9.0.

3. Conditions

The chemical usages and overall rates were varied. These are outlined in Tables 1 and 1-A. Where applicable, the codes for equivalent conditions in the batch process[3] are retained.

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TABLE 1

CONDITIONS OF EXPERIMENT

Chemical or Solution	Code	Usage
Overall rate, g. hexamine per minute	H_1	6.7
	H_2	13.5
	H_3	10.0
Paraformaldehyde used in first nitrator, g./g. hexamine	P_o	None
	P_1	0.16
	P_5	0.040
	P_6	0.020
	P_7	0.027
	P_8	0.054
	P'	--- (4 g. in heel only)
	P''	--- (8 g. in heel only)
Acetic acid used in first nitrator, g./g. hexamine (excluding heel)	D_1	1.63
	D_2	4.0
	D_3	9.0
Acetic anhydride used in first and second nitrators, g./g. hexamine (excluding heel)	A_2	3.17 + 4.75 = 7.92
	A_4	3.80 + 5.70 = 9.50
	A_8	3.80 + 2.87 = 6.67
	A_9	3.96 + 5.70 = 9.66
	A_{10}	3.96 + 4.46 = 8.42
	A_{11}	5.54 + 8.02 =13.56
	A_{12}	5.02 + 7.23 =12.25
	A_{13}	6.04 + 7.43 =13.47
HNO_3-NH_4NO_3 used in first and second nitrators, g./g. hexamine (R_2 = 51.7% HNO_3; R_3, R_4, R_5 = 56.4% HNO_3; R_6 = 70% HNO_3)	R_2	1.78 + 2.68 = 4.46
	R_3	1.63 + 2.46 = 4.09
	R_4	1.78 + 2.68 = 4.46
	R_5	2.28 + 3.42 = 5.70
	R_6	1.28 + 2.13 = 3.41

TABLE 1-A

COMPARISON OF NITRIC ACID-AMMONIUM NITRATE LEVELS

Chemical	Code	Usage
HNO_3 used in first and second nitrators, g./g. hexamine	R_2	0.92 + 1.39 = 2.31
	R_3	0.92 + 1.39 = 2.31
	R_4	1.00 + 1.51 = 2.51
	R_5	1.29 + 1.93 = 3.22
	R_6	0.90 + 1.49 = 2.39
NH_4NO_3 used in first and second nitrators, g./g. hexamine	R_2	0.86 + 1.29 = 2.15
	R_3	0.71 + 1.07 = 1.78
	R_4	0.78 + 1.17 = 1.95
	R_5	0.99 + 1.49 = 2.48
	R_6	0.38 + 0.64 = 1.02

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D. Results

The experimental results are summarized in Tables 2, 3, 4, and 5. Additional data are presented in Tables I and II of the Appendix. For several runs reported in Table 3 the use of each chemical or solution was determined both by weighing and by calculations based on the flow rates through the rotameters. Less than one percent variation was found in the two methods. Where applicable, usages and yields are based on rotameter data.

Data were collected during a portion of nine runs for the determination of the overall heat transfer coefficients and the heat loads which are presented in Table 6.

A factorial experiment consisting of Runs V-4, V-0, KK-0, and KK-4 is included in Table 4. The variables were the paraformaldehyde (P_0 and P_8) and acetic anhydride (A_4 and A_{11}) levels. Other conditions were constant at $R_3 D_3 H_3$. Continuous nitrators of design II were used. Statistical analysis showed no significant differences in product purity or pure yield at 95% Confidence Limits.

TABLE 2

SUMMARY OF RESULTS USING SEMI-CONTINUOUS NITRATORS

Run	Conditions	Av. Purity, %HMX	Av. Pure Yield, g. HMX/g. hex.	Product Filterability, min./gal.	Remarks
A-1	$P'A_{10}R_2D_1H_1$	89.1	.75	--	Slurry gelled in 2nd nitrator.
A-2	$P'A_{10}R_2D_1H_1$	93.3	.69	--	Slurry gelled in 2nd nitrator.
A-3	$P'A_{10}R_2D_1H_1$	91.1	.72	--	Slurry gelled in 2nd nitrator.
A-4	$P'A_{10}R_2D_1H_1$	99.0	.76	--	Slurry gelled in 2nd nitrator.
B-1	$P'A_{10}R_2D_1H_1$	97.2	.98	--	Temp. of 2nd nitrator hard to control. Gelling in 2nd nitrator very bad.
C-1	$P'A_{10}R_2D_2H_1$	87.1	1.14	--	Temp. control in 2nd nitrator good. No gelling. Coating bad in 2nd nitrator.
C-2	$P'A_{10}R_2D_2H_1$	87.8	1.12	8 to 16	
D-1	$P'A_{10}R_2D_2H_1$	85.5	1.37	8 to 16	Same as Run C-1. Started using HOAc to wash out collection pot with each batch.
D-2	$P'A_{10}R_2D_2H_1$	85.1	1.34	8 to 16	Same as Run C-1.
E-1*	$P'A_{10}R_2D_2H_1$	--	No product obtained	--	Legs of jeep plugged after 50 minutes of jeep operation.
F-1*	$P'A_{10}R_2D_2H_1$	--	No product obtained	--	Increased heel in jeep. Legs plugged after 75 minutes of jeep operation.
G-1*	$P'A_{10}R_2D_2H_1$	--	No product obtained	--	Increased heel in jeep. Legs plugged after 90 minutes of jeep operation.

*Note: In Runs E-1, F-1, and G-1 the jeep was used as the second nitrator.

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TABLE 3

SUMMARY OF RESULTS USING NITRATORS OF DESIGN I

Run	Conditions	Av. Purity, %HMX	Av. Pure Yield, g. HMX/g. hex.	Product Filterability, min./gal.	Remarks
H-1	$P''A_{10}R_4D_2H_2$	87.1	1.21	--	Leak in a feed line caused shutdown after 90 minutes of operation.
I-1	$P_5A_{10}R_4D_2H_2$	75.9	1.20	8 to 16	Slurry very thick in collection pot. Good temperature control in 2nd nitrator. Slight coatings in 1st nitrator and 1st age pot.
J-1*	$P_6A_8R_3D_3H_1$	72.4	1.15	8 to 16	Product in collection pot not as thick as when D_2 was used. Coating unchanged in 1st nitrator and 1st age pot.
J-2*	$P_6A_8R_3D_3H_1$	77.1	1.29	8 to 16	Same as Run J-1.
J-3*	$P_6A_8R_3D_3H_1$	74.5	1.12	8 to 16	Same as Run J-1.
K-1*	$P_5A_4R_3D_3H_1$	51.6	.83	4 to 8	Good filterability due to low purity.
JJ-1	$P_6A_8R_3D_3H_1$	76.1	1.09	8 to 16	Some coating in 1st nitrator and 1st age pot.
KK-1	$P_5A_4R_3D_3H_1$	53.2	.83	4 to 8	Good filterability due to low purity.
L-1	$P''A_4R_3D_2H_1$	78.6	1.44	8 to 16	Coating in 1st nitrator and 1st age pot was excessive. Slurry very thick in 2nd nitrator.
L-2	$P''A_4R_3D_2H_1$	83.5	1.28	8 to 16	Same as Run L-1.

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TABLE 3 (Contd.)

SUMMARY OF RESULTS USING NITRATORS OF DESIGN I

Run	Conditions	Av. Purity, %HMX	Av. Pure Yield, g. HMX/g. hex.	Product Filterability, min./gal.	Remarks
110-hr Run	$P_5A_8R_3D_3H_1$	86.6	1.29	8 to 16	See Table II of the Appendix.
JJ-2	$P_6A_8R_3D_3H_1$	88.7	1.30	--	Breakage of drive belts caused premature shutdown.
JJ-3	$P_6A_8R_3D_3H_1$	84.4	1.22	8 to 16	Same as Run JJ-1.
M-1	$P'A_8R_3D_3H_1$	83.8	1.34	8 to 16	Slightly less coating than for Run JJ-3.
M-2	$P'A_8R_3D_3H_1$	84.5	1.32	8 to 16	Same as Run M-1.
KK-2	$P_6(A_4-A_9)R_3D_3H_1$	91.1	1.42	8 to 16	Changing from A_4 to A_9 during the run decreased coating in 1st nitrator and 1st age pot.
N-1	$P_6A_{10}R_4D_3H_1$	89.2	1.33	8 to 16	Some coating in 1st nitrator and 1st age pot.
N-2	$P_6A_{10}R_4D_3H_1$	95.4	1.34	8 to 16	Same as Run N-1.

*Note: Runs J-1, J-2, J-3, and K-1 were made without the 1st age pot. The effluent from the 1st nitrator flowed into the 2nd nitrator.

TABLE 4

SUMMARY OF RESULTS USING NITRATORS OF DESIGN II

Run	Conditions	Av. Purity, %HMX	Av. Pure Yield, g. HMX/g. hex.	Product Filterability, min./gal.	Remarks
O-1	$P''A_{10}R_4D_2H_2$	89.3	1.11	8 to 16	Teflon scrapers removed coating from nitrator walls very well.
O-2	$P''A_{10}R_4D_2H_2$	94.5	1.06	8 to 16	Same as Run O-1.
P-1	$P_6A_{10}R_4D_2H_2$	90.7	1.12	8 to 16	Same as Run O-1.
Q-1	$P''A_{11}R_5D_3H_3$	73.0	.84	4 to 8	Product was beta HMX. Batches very thin in 2nd age and simmer. Practically no coating.
Q-2	$P''A_{11}R_5D_3H_3$	71.2	.773	4 to 8	Same as Run Q-1.
R-1	$P_7A_{11}R_5D_3H_3$	77.5	.875	4 to 8	Product was beta HMX. Slightly more coating in 1st nitrator.
S-1	$P_oA_{11}R_5D_3H_3$	71.0	.796	4 to 8	Product was beta HMX.
T-1	$P_oA_{13}R_5D_3H_3$	73.0	.718	4 to 8	Product was beta HMX.
U-1	$P_8A_4R_5D_3H_3$	86.8	1.10	4 to 8	Product was a mixture of alpha and beta HMX. Coating tendency increased.
V-1	$P_8A_{11}R_3D_3H_3$	86.3	1.57	3 to 4	Product was large alpha HMX. Practically no coating. Product slurry very thick. Product very fluffy when dry. Alpha crystals were 90 microns long and 4 microns wide. Impact sensitivity was normal (30 cm)

TABLE 4 (Contd.)

SUMMARY OF RESULTS USING NITRATORS OF DESIGN II

Run	Conditions	Av. Purity, %HMX	Av. Pure Yield, g. HMX/g. hex.	Product Filterability, min./gal.	Remarks
V-2	$P_8A_{11}R_3D_3H_3$	84.3	1.52	3 to 4	Same as Run V-1.
V-3	$P_8A_{11}R_3D_3H_3$	85.8	1.53	3 to 4	Same as Run V-1.
W-1	$P_7A_{11}R_3D_2H_3$	93.6	1.33	8 to 16	Alpha HMX was smaller in particle size. Coating tendency increased.
X-1	$P_7A_{11}R_5D_2H_3$	<10	.099	4 to 8	Good filterability due to very low purity.
KK-3	$P_6A_4R_3D_3H_2$	80.0	1.32	8 to 16	Slight coating tendency in all vessels.
Y-1	$P_5A_{12}R_3D_3H_2$	87.5	1.64	40 to 60	Product contained alpha and beta HMX. Practically no coating. Slurry hard to filter: 2 hr. to filter and wash a 2.5 gallon batch.
V-4*	$P_8A_{11}R_3D_3H_3$	88.2	1.44	3 to 4	Slurry easy to filter: 10 minutes to filter and wash a 2.5-gallon batch.
V-O*	$P_0A_{11}R_3D_3H_3$	83.8	1.43	3 to 4	Practically no coating.
KK-O*	$P_0A_4R_3D_3H_3$	82.9	1.42	8 to 16	Same as Run KK-3.
KK-4*	$P_8A_4R_3D_3H_3$	85.5	1.37	8 to 16	Same as Run KK-3.
Y-2	$P_5A_{12}R_3D_3H_2$	87.5	1.62	40 to 60	Same as Run Y-1.

TABLE 4 (Contd.)

SUMMARY OF RESULTS USING NITRATORS OF DESIGN II

Run	Conditions	Av. Purity, %HMX	Av. Pure Yield, g. HMX/g. hex.	Product Filterability, min./gal.	Remarks
Z-1	$P_oA_{11}R_6D_3H_3$	93.8	1.09	4 to 8	Product was medium sized alpha HMX.
Y-0	$P_oA_{12}R_3D_3H_2$	90.6	1.51	40 to 60	Same as Run Y-1.
VP-1	$P_oA_{11}R_2D_3H_3$	93.6	1.33	3 to 4	Product was large alpha HMX. Practically no coating.
AP-1	$P_1A_2R_2D_3H_3$	87.3	1.29	8 to 16	Coating tendency increased.
BV-1**	$P_oA_{11}R_3D_3H_3$	95.8	1.39	3 to 4	Good control of temperature and feed rates.
BV-2**	$P_oA_{11}R_3D_3H_3$	--	--	--	Run stopped due to power failure.
BV-3**	$P_oA_{11}R_3D_3H_3$	90.3	1.52	3 to 4	Same as Run BV-1.

*Note: Runs V-4, V-0, KK-0, and KK-4 constituted a factorial experiment.

**Note: In Runs BV-1, BV-2, and BV-3 the hexamine-acetic acid solution contained 62% acetic acid. A separate stream of acetic acid was fed to the 1st nitrator to obtain an overall usage of 9.0 g. acetic acid per g. hexamine.

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TABLE 5

SUMMARY OF RESULTS USING NITRATORS OF DESIGN III

Run	Conditions	Av. Purity, %HMX	Av. Pure Yield, g. HMX/g. hex.	Product Filterability min./gal.	Remarks
VJ-1	$P_0A_{11}R_3D_3H_3$	84.4	1.47	3 to 4	Jeep legs had a very thin hard crystal-line coating on the inside at end of run.
VJ-2	$P_0A_{11}R_3D_3H_3$	82.8	1.58	3 to 4	Jeep was operated longer than in Run VJ-1 but coating in legs was no thicker.
AJ-1	$P_8A_{11}R_3D_3H_3$	81.7	1.46	3 to 4	Same as VJ-1.

Note: In the above runs the hexamine-acetic acid solution contained 62% acetic acid. A separate stream of acetic acid was fed to the 1st nitrator to obtain an overall usage of 9.0 g. acetic acid per g. hexamine.

TABLE 6

SUMMARY OF THERMAL DATA

Run No.	Vessel	Continuous Nitrator Design	Overall Heat Transfer Coefficient B.t.u./hr.-ft.^{2}-$^\circ$F.
JJ-2	1st Nitrator	I	45
JJ-3	1st Nitrator	I	46
JJ-3	1st Age Pot	I	5.5
JJ-3	2nd Nitrator	I	42
O-2	1st Nitrator	II	75*
V-3	1st Nitrator	II	76*
X-1	1st Nitrator	II	38
BV-3	1st Nitrator	II	113*
AJ-1	1st Nitrator (jeep)	III	69

*Note: The cooling water used in Runs O-2, V-3, and BV-3 was preheated to permit increased usage and velocity through the nitrator jacket. The jacket of 1st nitrator was cleaned with 10% HCl prior to Run BV-3.

Based on the data from Batch 2 of Run JJ-3, the apparent heat of reaction and the relative heat load for each vessel was calculated:

Nitration Conditions:	$P_6A_8R_3D_3H_1$ (Design I)
Product Purity:	82.7% HMX
Pure Yield:	1.20 g. pure HMX/g. hexamine
Apparent Heat of Reaction:	1503 B.t.u./lb. crude HMX

Percent of Total Heat Load Removed In:

First Nitrator	62
First Age Pot	7
Second Nitrator	28
Collection Pot (2nd Age)	3
	100

Note: The apparent heat of reaction is corrected for estimated radiation losses but not feed conditions.

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III. DISCUSSION OF RESULTS

A. Equipment Considerations

The semi-continuous nitration equipment used in the first phase of the project was selected because of its availability and usefulness as interim equipment. No particular significance is attached to its design other than it approximated the desired size and permitted manual removal of most of the material which coated the wetted surfaces.

Attempts to use the jeep as a second nitrator were unsuccessful. This was due to the tendency of the slurry to rapidly deposit HMX on the cooling surfaces. Temperature control became impossible. The slurry gelled and the cooling legs plugged completely in relatively short periods even though the heel of acetic acid had not been completely displaced. It is believed that increased acetic acid and acetic anhydride levels in the feeds and the resultant thinner slurry would have permitted somewhat longer periods of operation. However, a slurry of very small particles of HMX has little tendency to scavenge a coat of HMX from a surface. This characteristic would have prevented satisfactory operation.

Excessive coating dictated some means of preventing or removing the coating from the cooling surfaces of the second nitrator. Since preventive means were lacking, the second nitrator of Design I was equipped with a Teflon scraper which successfully removed excessive coating.

Previous experience and observations of semi-continuous nitration showed that the final nitration slurry thickened considerably with aging time. Since it had been observed that coating increased with the thickness of the slurry, the volume of the second nitrator was reduced as much as practicable to obtain minimum aging and thereby reduce this coating. The

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principal consideration in the design of the first nitrator and the first age pot of Design I was the hold-up time required for the initial aging period. Previous batch nitrations[3,4] had demonstrated the desirability for aging 15 minutes between the nitration stages.

Comparisons of the runs reported in Table 3 without a first age pot (Runs J-1, J-2, J-3, and K-1) with runs having comparable conditions and a first age pot (Runs JJ-1, JJ-2, JJ-3, KK-1, KK-2) show that improvement in purity and pure yield are not definitely indicated by the use of a first age pot. It is felt that the experience gained from the 110-hour run is largely responsible for the improved results of Runs JJ-2, JJ-3, and KK-2. However, in all of the above runs the total flow rates through the first nitrator were considerably lower than the rate used in Run V-O or comparable runs (see Table 4) in which optimum product purity, pure yield, and filterability were obtained. With the conditions of Run V-O calculations by the method of MacMullin and Weber[7] show that 94% of the material entering the first nitrator is retained at least 15 minutes before overflowing from the first age pot. It is believed that the first age pot is desirable at the higher flow rates.

Observations made during the 110-hour run (Table II of the Appendix) resulted in the eventual redesign of the first nitrator and the first age pot to utilize Teflon scrapers. The vessels were sized for the desired retention time.

The results of runs in Table 4 again demonstrated the effectiveness of the Teflon scraper in removing excessive coating. It was occasionally necessary to manually scrape the coating from the overflow tubes (down-spouts) and from the scraper assembly, particularly where the nitric acid-ammonium nitrate feed contacted the assembly above the liquid level

in the second nitrator. Therefore, any plant nitrators utilizing a
scraper should be designed to introduce the nitric acid solution away
from the scraper assembly. Further, the design should permit occasional
manual cleaning of the assembly, the upper portion of the vessel walls,
and the downspout. A device similar to the vertical downspout from the
Holston RDX nitrators would be effective in permitting the cleaning of
the downspout. The coating in the downspout from the first age pot can
be minimized by introducing the acetic anhydride through it into the
second nitrator.

Except for the runs in which low pure yields were obtained a coating
of HMX was deposited on the walls of the collection pot. This coating
has also been experienced in the pilot plant. In plant equipment the
coating can be removed by the use of a Teflon scraper in the collection
pot. Since experience has shown that simmering will remove a HMX coating,
an alternative is to utilize several tanks in parallel to collect the
effluent from the second nitrator. Final aging and simmering of a batch
would be effected in the tank used for collection of the batch.

Runs BV-1 and BV-3 reported in Table 4 and all runs reported in
Table 5 show that the desired acetic acid usage can be successfully
attained by feeding the hexamine solution containing 62% acetic acid
and admitting a separate stream of acetic acid. The use of a 62% acid
solution will minimize the cost of the hexamine dissolving step in a
process employing continuous nitration.

Since it has been observed that less coating occurred in the first
nitrator than in the second nitrator, the jeep was used as a first
nitrator in the runs listed in Table 5. These runs indicate that the

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jeep can be used successfully as the first nitrator when the acetic anhydride usage is high. However, the limited experimental data indicate that the purity of the crude product is decreased by the use of the jeep (Runs VJ-1, VJ-2, and AJ-1 vs Runs BV-1 and BV-3).

Although the legs of the jeep were coated slightly with rather hard crystalline material, the design was judged to be satisfactory with respect to coating. This opinion is based largely on experience with the RDX process in which the laboratory jeep is coated slightly while the plant jeep is not coated. This is attributed to the scavenging action of the RDX slurry under plant conditions. While the HMX in the second nitrator has virtually no scavenging properties, the particles of the intermediate product in the first nitrator appear to be large enough to be somewhat abrasive. Furthermore, several checks on the cooling water rates and temperatures showed no reduction in the cooling capacity of the jeep after the initial coating occurred. It is postulated that the abrasive action of the intermediate product would prevent a build-up of coating in a HMX plant scale jeep having adequate slurry velocity through the cooling leg.

It is doubtful that the lower acetic anhydride levels would permit the use of a jeep as the first nitrator. Reduced acetic anhydride usage decreases the fluidity of the material in the first nitrator and increases its coating tendency. Smaller particles having less abrasive properties would also be anticipated.

All other considerations being equal, the jeep would be preferable to a jacketed vessel because of its high heat transfer area per unit volume. The jeep will probably facilitate plant designs of the first nitrator and first age pot based on the required retention time and,

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therefore, permit minimum explosive loads in the plant. In view of the slight coating and apparent decrease in purity with the laboratory jeep it is recommended that final selection of the type of first nitrator be made after pilot plant trials of a jeep and a jacketed vessel similar to Design II.

B. Nitration Conditions

Although the design of equipment to produce HMX continuously was the primary purpose of this project, much work was done to determine optimum nitration conditions from the standpoint of product purity, pure yield, filterability, and coating properties. The initial work done with the semi-continuous nitrators utilized conditions established since the issuance of the latest HMX report.[3]

The results of the runs listed in Table 2 show that increased acetic acid is required for the prevention of gelling. With 1.63 g. HOAc per g. hexamine (a solution containing 62% HOAc) the slurry in the second nitrator became so thick that it would not overflow. Due to the rapid coating of cooling surfaces precise temperature control was impossible. The difficulties were alleviated somewhat by increasing the acetic acid usage to 4.0 g. per g. hexamine (equivalent to 80% HOAc in the hexamine solution).

The runs summarized in Table 3 show that to obtain adequate fluidity of the final nitration slurry, 9.0 g. HOAc per g. hexamine (or 90% HOAc in the hexamine solution) is desirable at the acetic anhydride levels used. The coating tendency is also reduced in all nitration vessels by the increased acetic acid usage.

Even when the higher acetic anhydride levels were used (Table 4), coating was decreased and both pure yield and filterability were

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improved by the use of 9.0 g. HOAc/g. hexamine as compared with 4.0 g. HOAc/g. hexamine. Although the latter tended to give higher product purity, it is judged that the higher acetic acid level is more desirable in this case. It is significant to note that the laboratory batch process employs 9.4 g. acetic acid per g. hexamine while a ratio of 6.5 to 1 is used in the pilot plant.

Of the many acetic anhydride levels used in the experimental runs, the level which produced the highest average pure yield (1.59 g. pure HMX/g. hexamine) was A_{12} which was 12.25 g. Ac_2O per g. hexamine. But the product filterability was very poor, filtering and washing the product in a 2.5-gallon batch requiring about two hours. In the Y-series of runs which utilized the R_3A_{12} levels the product contained roughly a 50-50 mixture of the alpha and beta polymorphs of HMX, both relatively small in crystal size. The product purity averaged 88.5% HMX.

Use of the acetic anhydride level A_{11} (13.56 g. Ac_2O per g. hexamine) gave the most easily filtered product with high purity, the second best pure yield, and a minimum of coating. When the R_2A_{11} and R_3A_{11} levels were used the HMX produced consisted of relatively large particles of the alpha polymorph, approximately 90 microns in length and 4 microns in width. The product in a 2.5-gallon batch could be filtered and washed in less than 10 minutes. The impact sensitivity of the product was normal at 30 cm. for 50% detonation with a 5-kg. weight.

With the exceptions mentioned above or unless noted otherwise in the tables of results, the HMX in the crude product was in the form of the alpha polymorph averaging about 8 microns in length and 1 micron in width.

The remaining acetic anhydride levels had an adverse affect on filterability and coating and did not improve purity or yield.

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The results of the several runs reported in Table 4 which utilized varying nitric acid and ammonium nitrate levels indicate that R_2 and R_3 are preferable to R_4, R_5, or R_6 (See Table 1A). The current results indicate, and previous batch-wise work yet to be published shows that R_3 is preferable to R_2 in terms of pure yield when the acetic anhydride level is 9.5 parts per part of hexamine. Since R_2 and R_3 are equal in nitric acid usage and R_2 uses more ammonium nitrate, the R_3 level is economically desirable.

The factorial experiment reported in Table 4 (Runs V-4, V-0, KK-0, and KK-4) shows, at 95% Confidence Limits, no significant difference in purity or pure yield to be caused by the paraformaldehyde or acetic anhydride levels tested. The difference in purity is significant at the 85% Confidence Level, the higher purity being associated with the higher paraformaldehyde level. Previously published work[3] has shown paraformaldehyde to improve purity at the lower anhydride levels. Runs Y-1, Y-2, Y-0 and the results in Table 5 tend to refute the effect. Based on this and batch-wise work yet to be published, it is submitted that the effect of using paraformaldehyde is virtually nil when the higher acetic anhydride levels are used. Due to the raw material and handling costs, toxicity, and doubtful effectiveness of paraformaldehyde, its use is not recommended with high acetic anhydride levels.

It may be of interest to note that attempts to dissolve paraformaldehyde in the nitrator feeds at the level equivalent to P_6 were unsuccessful.

As shown in the above discussion, the recommended conditions for continuous HMX nitration are $P_0A_{11}R_3D_3$. The results of runs utilizing these conditions are as follows.

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Run	Av. Product Purity, %HMX	Av. Pure Yield, g. HMX/g. Hexamine
V-0	83.8	1.43
BV-1	95.8	1.39
BV-3	90.3	1.52
VJ-1*	85.1	1.54
VJ-2	82.8	1.58
Weighted Average	86.8	1.50

*Note: Since the first batch in each run utilizing the jeep produced consistently lower yields than succeeding batches, the results from Batch 1 of Run VJ-1 were omitted in the averages listed. The apparent low yield of the first batch is attributed to the relatively large heel required for the jeep.

In runs Q-1, Q-2, R-1, S-1, and T-1 (see Table 4) the HMX produced was the beta polymorph. By comparison with Runs U-1, V-1, and X-1, it can be seen that very high acetic anhydride, nitric acid-ammonium nitrate, and acetic acid usages are required to obtain the beta form. Pilot plant experience has shown that crystallization is required to reduce the crystal acidity even when the HMX has previously been transformed to the beta polymorph. Since the conditions of the V-series of runs were more desirable in terms of product filterability, purity, and pure yield, the direct synthesis of beta HMX was studied only briefly.

C. Heat Loads

The low heat transfer coefficients listed in Table 6 are attributed to low film coefficients on the water or jacket side caused by short circuiting or even virtual stagnation of the cooling water. This is evidenced by the very low coefficient for the first age pot and by the increase in coefficient when the cooling water was warmed. Preheating the water permitted the use of more cooling water while maintaining the desired nitrator temperature. The increased water velocity and turbulence improved the overall coefficient. It is believed that a coefficient of at

least 75 B.t.u./hr.-ft.^{2}-^{o}F. would have been attained for each of the three vessels used had it been practical to increase the water turbulence in the jackets.

The apparent heat of reaction (1503 B.t.u./lb. crude HMX) reported in Table 6 has also been calculated to be 1626 B.t.u. per lb. of pure HMX. The calculation was made by deducting the heat attributed to RDX, at 927 B.t.u. per lb. as reported by Bassler,[8] and stating the resulting heat, attributed to HMX, on a pure HMX basis.

IV. SUMMARY

Hexamine can be continuously nitrated in two stages to produce HMX. The basic nitration equipment consists of a first nitrator, first age pot, second nitrator, and collection pot (final age pot). Using the conditions recommended below the crude product contains about 87% HMX and 13% RDX and has an impact sensitivity comparable to the crude HMX produced by the batch process. The yield obtained is 1.5 pounds of pure HMX per pound of hexamine which is 71% of theory.

A satisfactory design of the nitration equipment employs agitated, jacketed vessels which have a low speed Teflon scraper to remove excessive coating of the intermediates or the product on the cooling surfaces. Since the use of a jeep as the first nitrator also gave encouraging results, the final selection of the first nitrator design should be based on pilot plant work.

With 87% product purity the apparent heat of reaction approaches 1536 B.t.u. per pound of crude HMX. The heat load is distributed 62, 7, 28, and 3 percent respectively in the first nitrator, first age pot, second nitrator, and final age pot.

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The nitration conditions recommended are:

Nitration temperature (all stages): 44°C.

Initial aging time: 15 minutes

Final aging time: 60 minutes

Chemical usages per lb. hexamine:

	First Nitrator	Second Nitrator	Total
Acetic acid	9.0	---	9.0
Nitric acid*	0.92	1.39	2.31
Ammonium nitrate*	0.71	1.07	1.78
Acetic anhydride	5.54	8.02	13.56

*Equivalent to 56.4% nitric acid in a nitric acid-ammonium nitrate solution.

These conditions caused a minimum of coating of cooling surfaces and gave a product with improved filterability. The HMX produced is the alpha polymorph which is considerably larger in particle size than that obtained with other conditions. The recommended nitration conditions are essentially identical to those employed in the present pilot plant batch process at Holston.

The beta polymorph can be produced directly in the nitration step by increasing the nitric acid-ammonium nitrate usage to 5.70 pounds per pound of hexamine, but otherwise using the above recommended nitration conditions. However, the low product purity and pure yield make the method economically undesirable.

When the overall interest in HMX warrants the undertaking, a pilot plant trial of the continuous process and equipment design is recommended. The required experience and engineering data for the optimum design of large scale production equipment would then be acquired. Further, a pilot plant trial of the jeep design of the first nitrator is necessary before an unqualified recommendation as to its use can be made.

V. APPENDIX
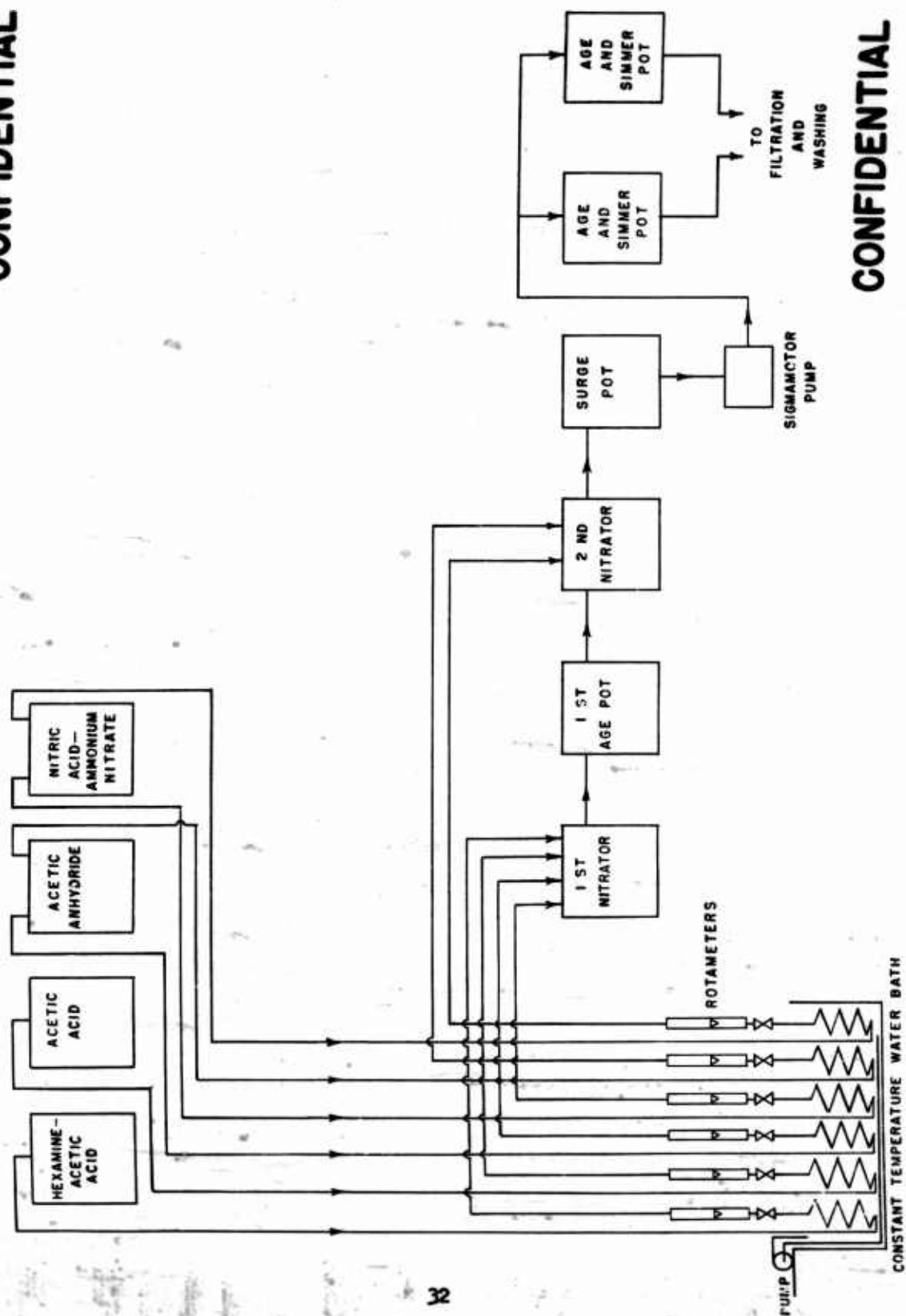
FIG I FLOW DIAGRAM OF CONTINUOUS HMX NITRATION

CONFIDENTIAL

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PLATE 1

SEMI-CONTINUOUS NITRATORS

33
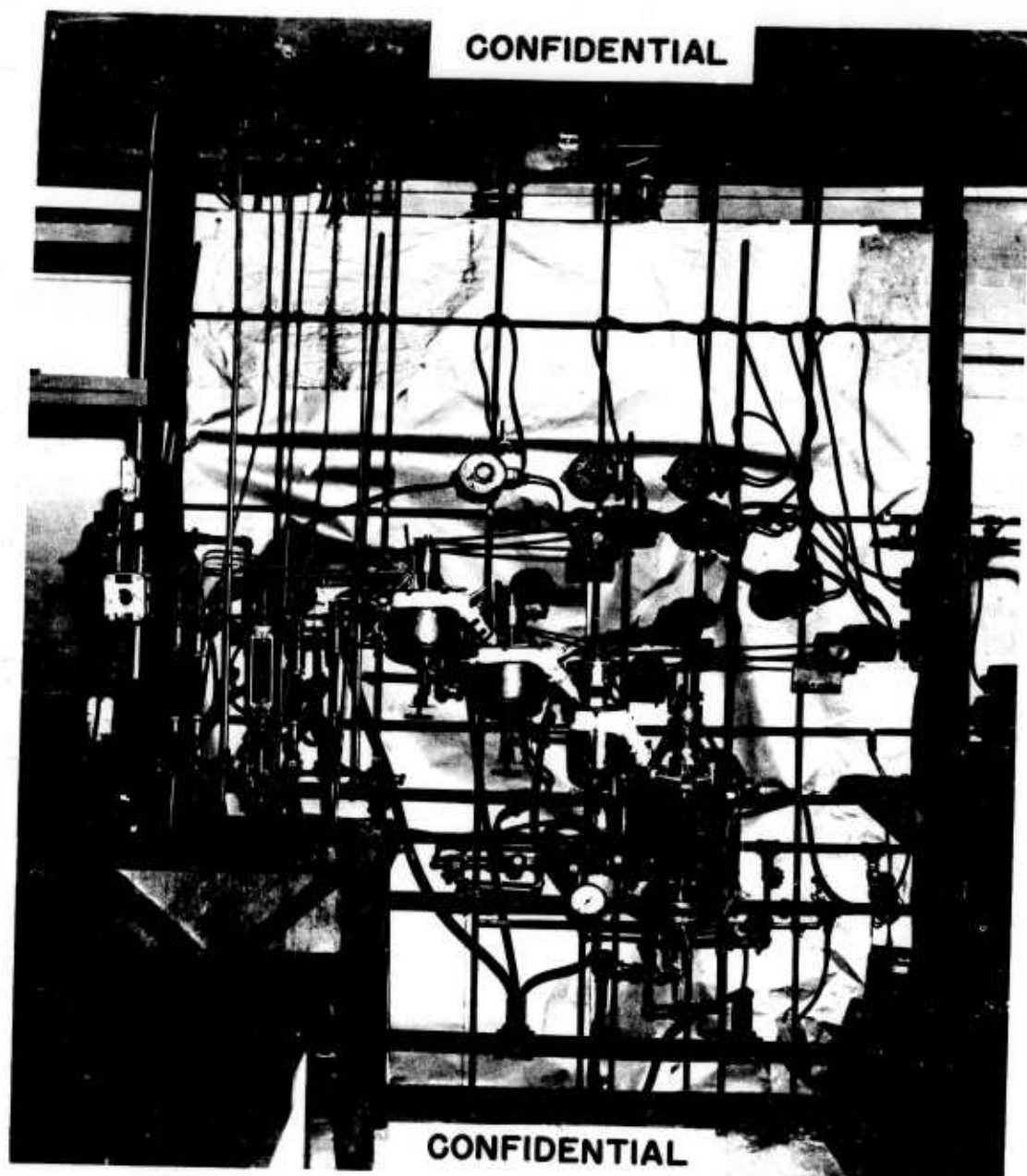
PLATE 2

CONTINUOUS NITRATORS - DESIGN I

NOTE:
POT DIA. – 6"
POT HEIGHT – 4.5"
8 BAFFLES – 1"X 1.5"

DOWNSPOUT

BAFFLES

COOLING JACKET

FIG. 2   1ST NITRATOR AND 1ST AGE POT
DESIGN I

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NOTE:
POT DIA.- 4"
POT HEIGHT- 4"
POT VOLUME- 1000 ML.

DOCTOR BLADE
SUPPORT

DOWNSPOUT
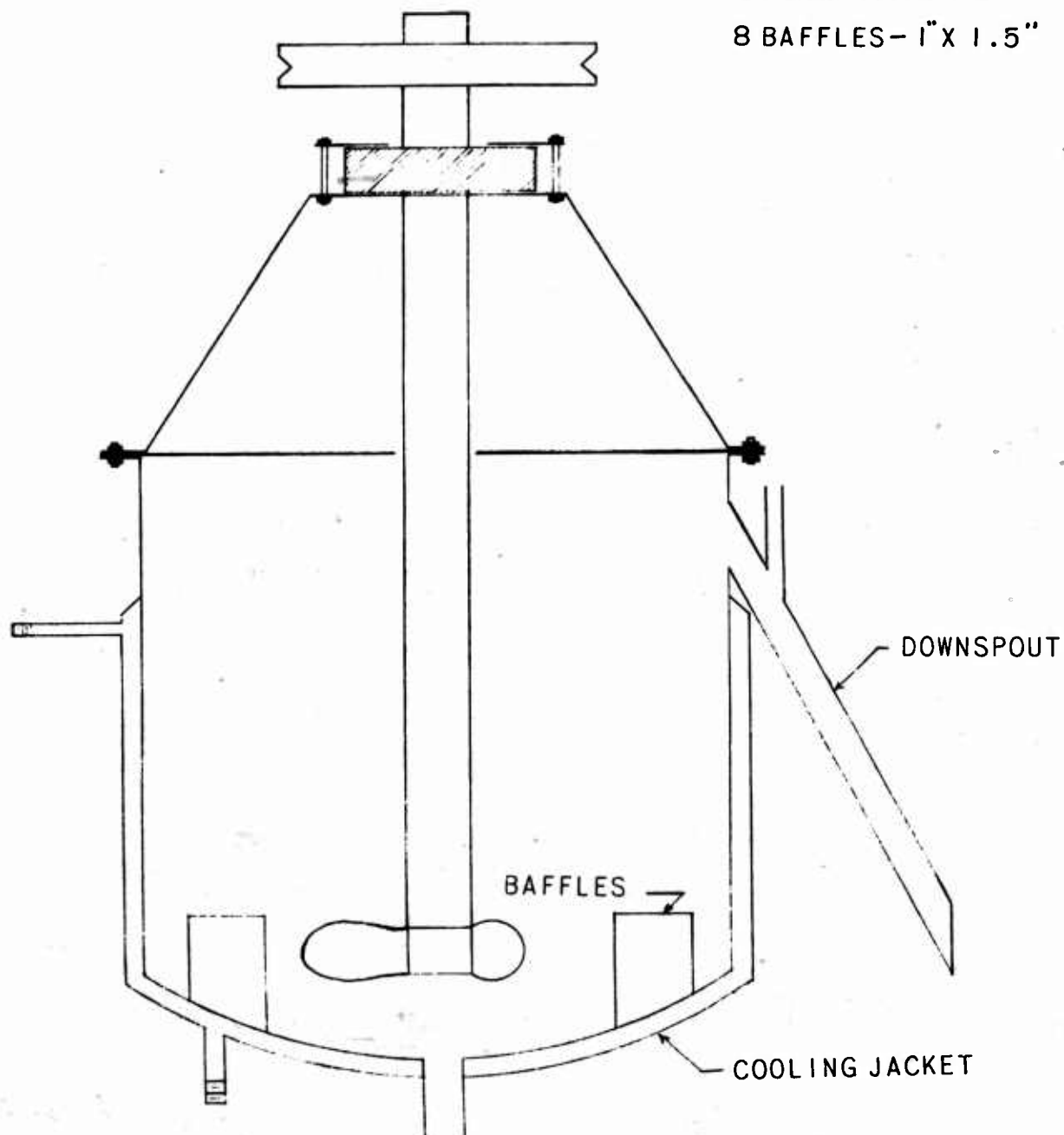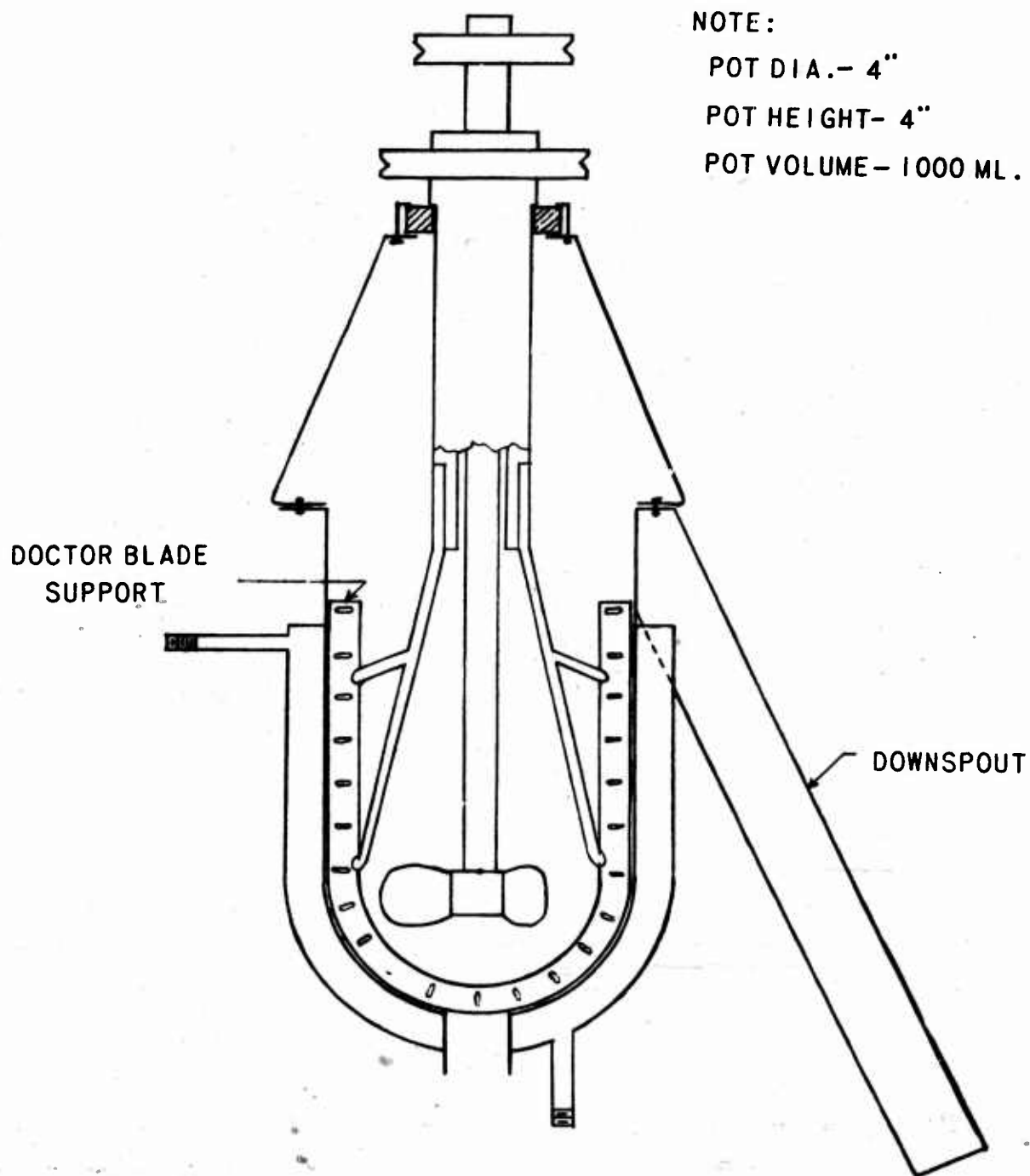
FIG. 3   2ND NITRATOR CONTINUOUS DESIGN

36
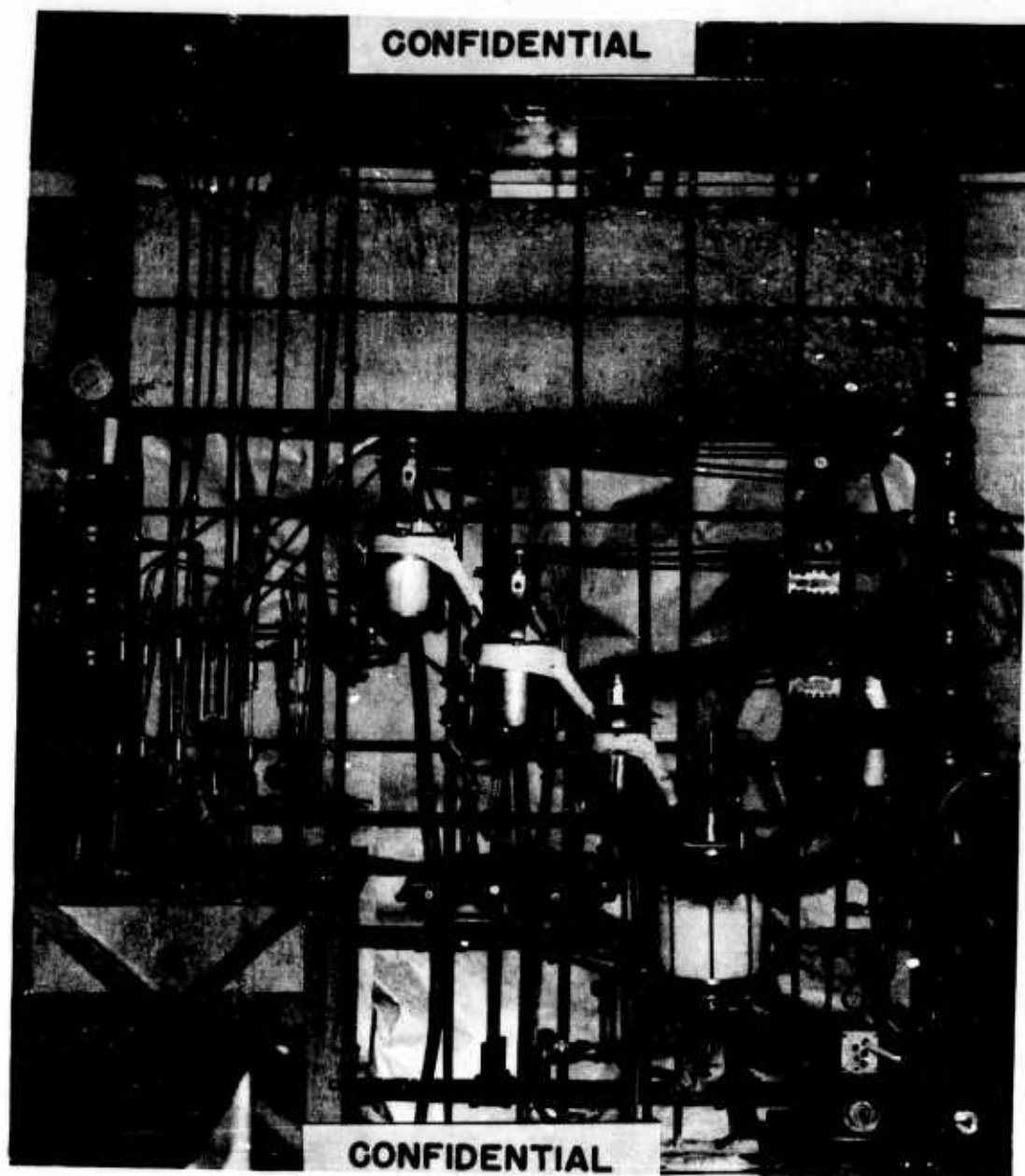
PLATE 3

CONTINUOUS NITRATORS - DESIGN II

CONFIDENTIAL

NOTE:
POT DIA.- 6"
POT HEIGHT- 6"
POT VOLUME - 2800 ML
BEARINGS (3)

DOWNSPOUT

COOLING JACKET
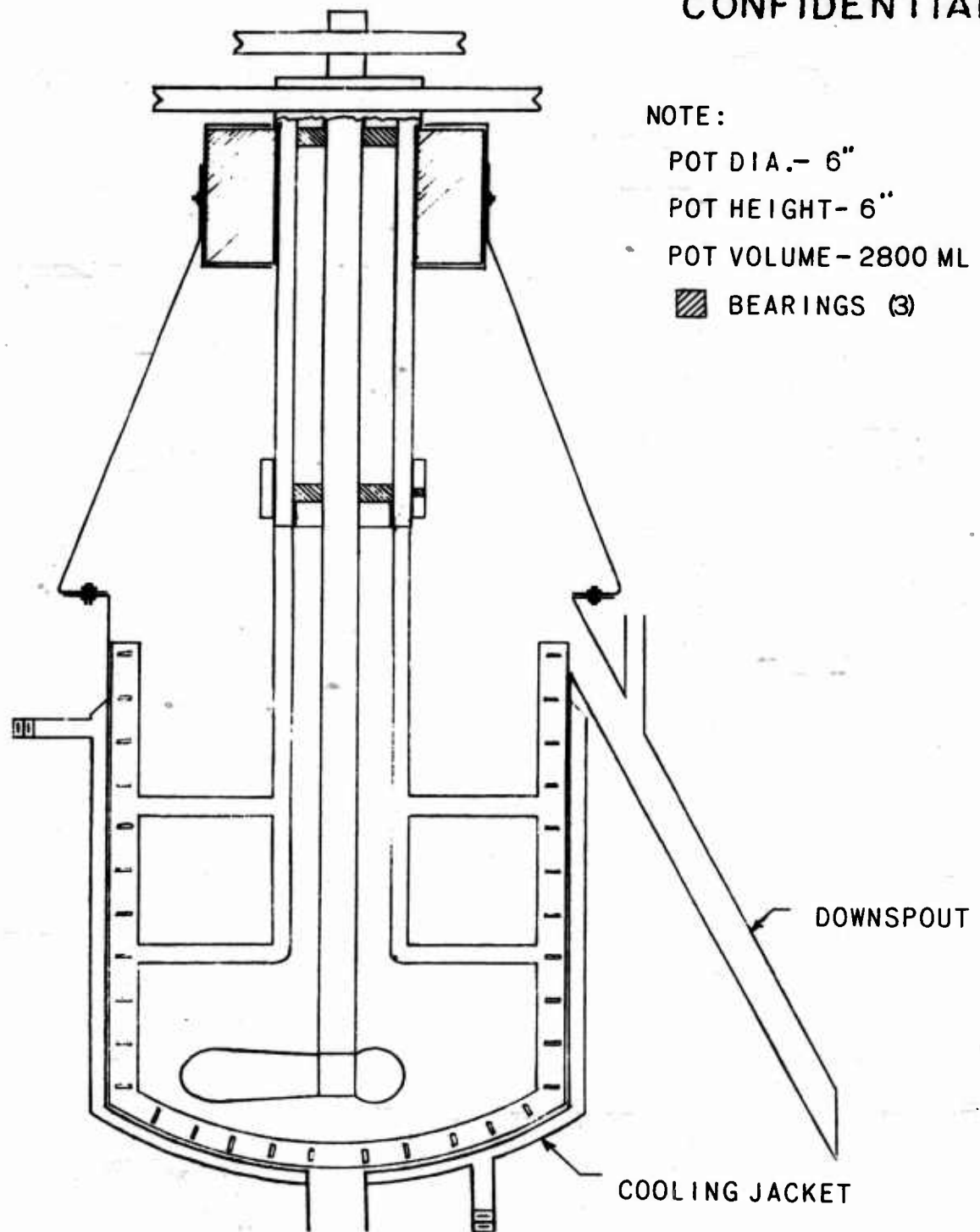
FIG. 4   1ST NITRATOR AND 1ST AGE POT
DESIGN II

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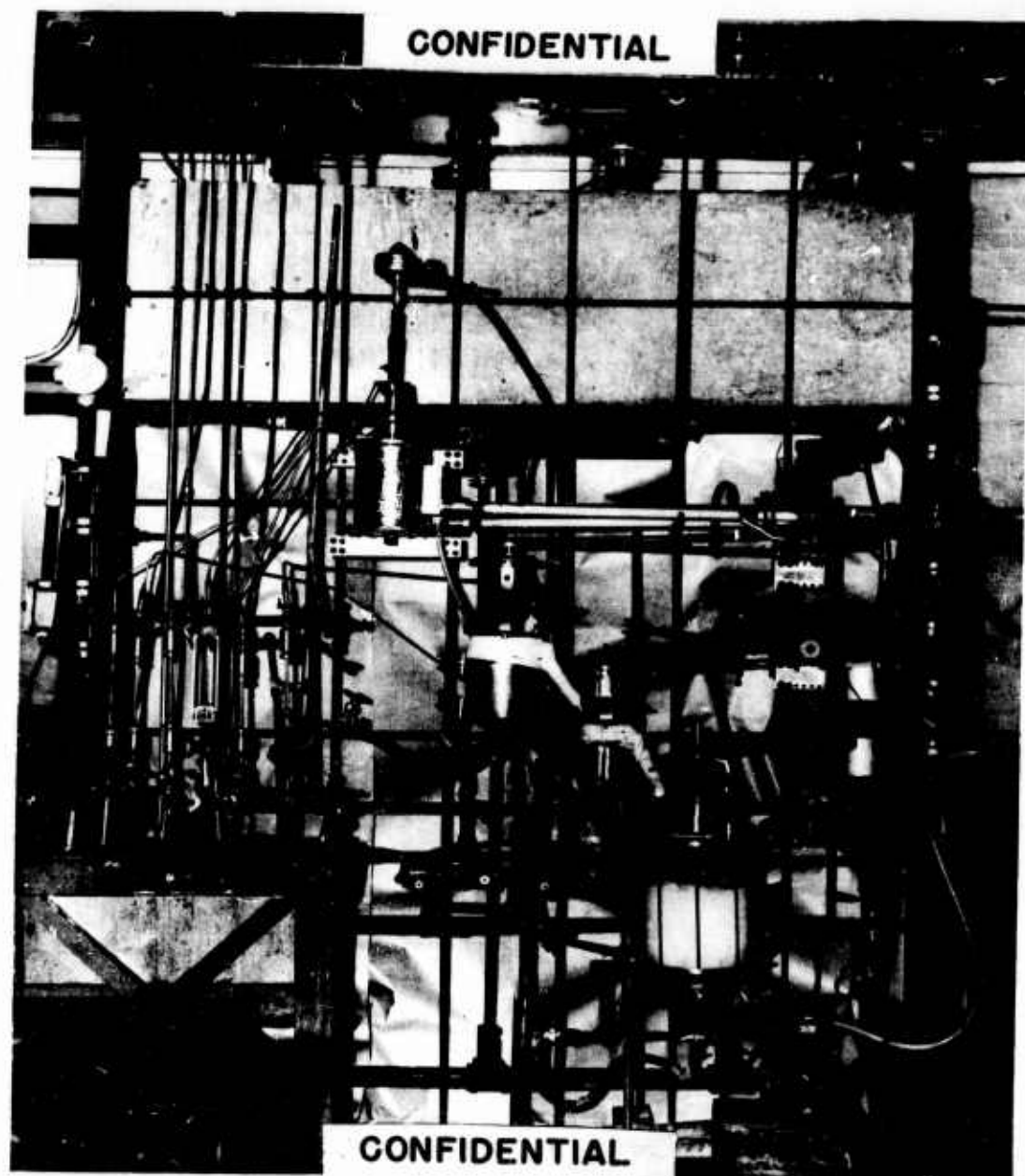
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PLATE 4

CONTINUOUS NITRATORS - DESIGN III

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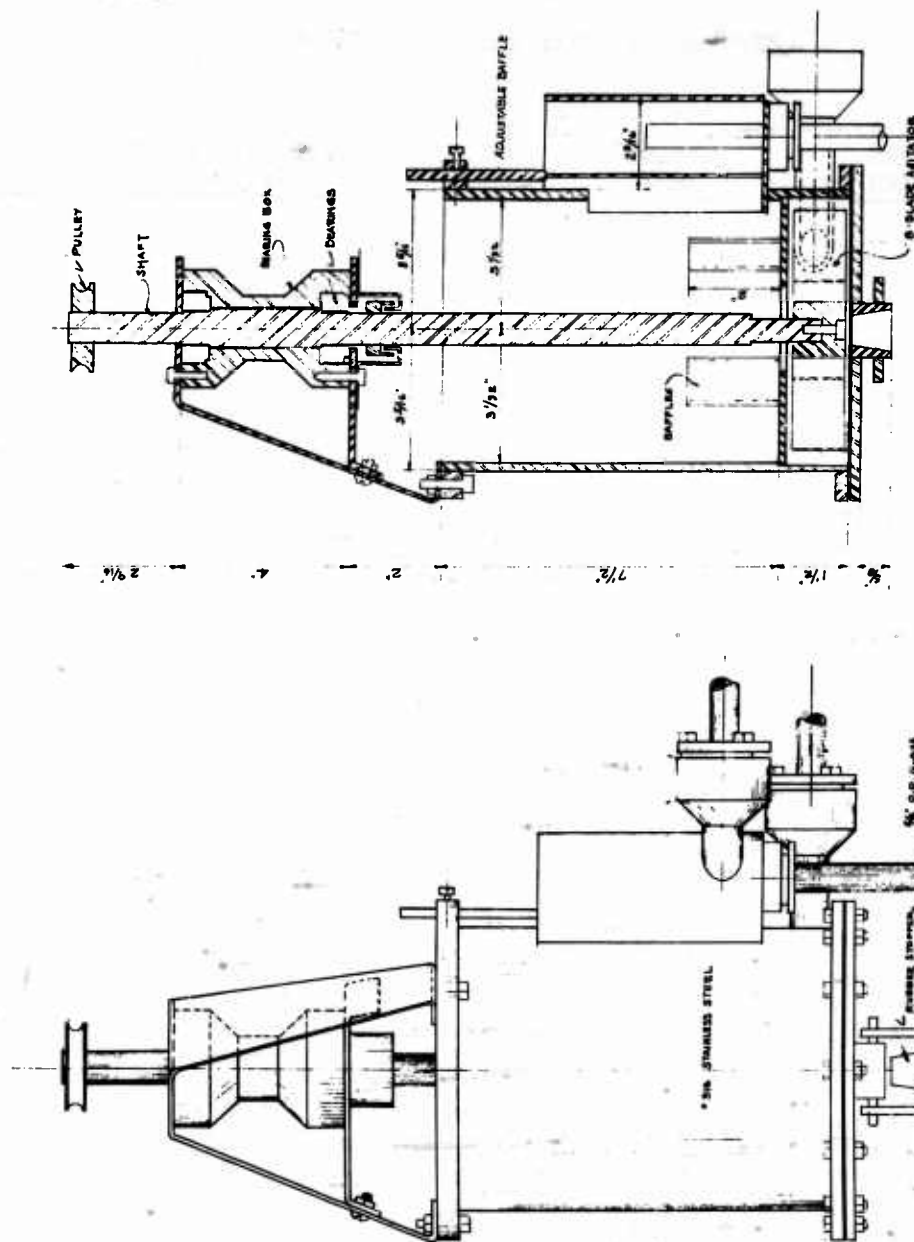
FIG. 5 ISJ NITRATOR (JEEP) DESIGN III

SECTION

ELEVATION

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TABLE I

PURITY AND PURE YIELD OF BATCHES

Run	Collection Time, min./batch	Batch	Purity, %HMX	Pure Yield, g. HMX/g. hexamine
A-1	45	1	89.1	0.75
A-2	45	1	93.3	0.69
A-3	45	1	91.1	0.72
A-4	45	1	99.0	0.76
B-1	30	1	97.2	0.98
C-1	30	1	87.1	1.14
C-2	30	1	87.6	0.98
	30	2	88.0	1.11
	30	3	87.7	1.27
D-1	30	1	86.4	1.34
	30	2	86.4	1.30
	30	3	86.8	1.41
	30	4	79.2	1.20
	30	5	88.7	1.62
D-2	30	1	86.2	1.20
	30	2	82.8	1.23
	30	3	83.5	1.46
	30	4	85.2	1.17
	30	5	87.6	1.63
H-1	30	1	87.1	1.21
I-1	30	1	74.8	1.20
	30	2	74.1	1.13
	30	3	72.3	1.20
	30	4	77.2	1.13
	30	5	76.8	1.22
	30	6	80.1	1.77

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TABLE I (Contd.)

Run	Collection Time, min./batch	Batch	Purity, %HMX	Pure Yield, g. HMX/g. hexamine
J-1	60	1	72.4	1.14
	60	2	73.5	1.11
	60	3	71.3	1.21
J-2	60	1	76.8	1.13
	60	2	77.1	1.47
	60	3	77.5	1.32
J-3	60	1	70.7	1.06
	60	2	77.7	1.15
	60	3	75.2	1.16
K-1	60	1	53.6	0.84
	60	2	46.9	0.71
	60	3	54.2	0.95
JJ-1	60	1	60.1	0.81
	60	2	84.7	1.15
	60	3	79.7	1.25
	60	4	79.9	1.14
KK-1	60	1	66.3	1.01
	60	2	49.9	0.81
	60	3	41.7	0.64
	60	4	43.2	0.65
	60	5	64.8	1.03
L-1	60	1	75.9	1.48
	60	2	80.0	1.45
	60	3	80.0	1.39
L-2	60	1	89.2	1.22
	60	2	81.3	1.36
	60	3	79.9	1.26
JJ-2	60	1	88.7	1.30
JJ-3	60	1	83.6	1.18
	60	2	82.7	1.20
	60	3	87.0	1.29
M-1	60	1	81.3	1.28
	60	2	85.9	1.32
	60	3	84.3	1.43

TABLE I (Contd.)

Run	Collection Time, min./batch	Batch	Purity, %HMX	Pure Yield, g. HMX/g. hexamine
M-2	60	1	81.4	1.24
	60	2	85.8	1.28
	60	3	86.2	1.43
KK-2	60	1	92.5	1.32
	60	2	94.1	1.41
	60	3	86.8	1.52
N-1	60	1	89.9	1.24
	60	2	89.4	1.39
	60	3	88.4	1.37
N-2	60	1	97.6	1.27
	60	2	93.8	1.34
	60	3	94.8	1.41
O-1	30	1	87.0	1.08
	30	2	91.6	1.10
	30	3	89.4	1.14
O-2	30	1	94.2	1.02
	30	2	96.2	1.05
	30	3	93.1	1.10
P-1	30	1	86.7	1.23
	30	2	96.1	1.03
	30	3	89.3	1.11
Q-1	30	1	87.4	1.06
	30	2	71.3	0.744
	30	3	60.4	0.718
Q-2	30	1	86.0	0.78
	30	2	66.7	0.778
	30	3	60.8	0.762
R-1	30	1	94.8	0.96
	30	2	72.6	0.88
	30	3	65.1	0.784
S-1	30	1	82.3	0.90
	30	2	66.0	0.748
	30	3	64.7	0.74

TABLE I (Contd.)

Run	Collection Time, min./batch	Batch	Purity, %HMX	Pure Yield, g. HMX/g. hexamine
T-1	30	1	88.1	
	30	2	68.8	0.83
	30	3	62.1	0.685
				0.64
U-1	30	1	89.8	
	30	2	86.5	0.973
	30	3	84.5	1.11
				1.21
V-1	30	1	80.1	
	30	2	87.8	1.49
	30	3	91.1	1.58
				1.63
V-2	30	1	85.2	
	30	2	85.9	1.49
	30	3	82.4	1.54
	30	4	83.9	1.47
				1.56
V-3	30	1	85.4	
	30	2	87.5	1.50
	30	3	84.5	1.46
				1.63
W-1	40	1	89.1	
	40	2	94.7	---
	40	3	97.1	1.33
				1.33
X-1	40	1	< 10	
	40	2	< 10	0.096
	40	3	< 10	0.100
				0.102
KK-3	30	1	81.3	
	30	2	81.2	1.28
	30	3	77.5	1.38
				1.30
Y-1	30	1	88.5	
	30	2	89.5	1.63
	30	3	84.6	1.64
				1.66
V-4	30	1	90.4	
	30	2	88.0	1.39
	30	3	86.2	1.45
				1.47
V-0	30	1	85.4	
	30	2	83.0	1.38
	30	3	83.1	1.42
				1.49

TABLE I (Contd.)

Run	Collection Time, min./batch	Batch	Purity, %HMX	Pure Yield, g. HMX/g. hexamine
KK-0	30	1	81.7	1.36
	30	2	85.4	1.43
	30	3	81.7	1.47
KK-4	30	1	85.4	1.33
	30	2	86.9	1.38
	30	3	84.3	1.39
Y-2	30	1	84.9	1.54
	30	2	89.5	1.65
	30	3	88.1	1.66
Z-1	30	1	95.5	1.06
	30	2	92.1	1.11
Y-0	30	1	90.7	1.40
	30	2	91.3	1.58
	30	3	89.7	1.55
VP-1	30	1	89.4	1.34
	30	2	95.9	1.31
	30	3	95.5	1.34
AP-1	30	1	85.9	1.30
	30	2	87.0	1.29
	30	3	88.9	1.29
BV-1	30	1	94.7	1.39
	30	2	96.9	1.39
BV-3	30	1	94.3	1.61
	30	2	90.2	1.43
	30	3	86.5	1.52
VJ-1	30	1	83.0	1.31
	30	2	87.1	1.47
	30	3	83.1	1.62
VJ-2	30	1	--	--
	30	2	84.0	1.54
	30	3	--	--
	30	4	81.9	1.51
	30	5	--	--
	30	6	83.1	1.55
	30	7	82.0	1.71

TABLE I (Contd.)

Run	Collection Time, min./batch	Batch	Purity, %HMX	Pure Yield, g. HMX/g. hexamine
AJ-1	30	1	80.7	1.30
	30	2	83.0	1.51
	30	3	81.4	1.57

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TABLE II

RESULTS FROM 110-HOUR RUN

Running Time, Hr.	Conditions	Purity, %HMX	Pure Yield, g.HMX/g. hex.	Remarks
0-44	$P_5A_8R_3D_3H_1$	82.5 (av. of 11 batches)	1.30	Coating in all vessels very bad except where removed by Teflon scraper.
45-60	$P_5A_8R_3D_3H_1$	89.9 (av. of 4 batches)	1.24	Both Ac_2O usages increased 1.1 g./min. Coating decreased slightly.
61-70	$P_5A_8R_3D_3H_1$	89.0 (av. of 2 batches)	1.15	Ac_2O to 1st nitrator now 2.2 g./min. high; 2nd nitrator normal A_8.
71	$P_5A_8R_3D_3H_1$	--	--	Ac_2O to both nitrators now 1.1 g./min. high.
72-74	$P_6A_8R_3D_3H_3$	91.4	1.26	Ac_2O to 1st nitrator 1.1 g./min. low; to 2nd nitrator 1.1 g./min. high. Batches much thicker than usual.
75-80	$P_6A_8R_3D_3H_1$	85.2 (av. of 2 batches)	1.41	Ac_2O to 1st nitrator 3.3 g./min. high; to 2nd nitrator 3.3 g./min. low. Batches thicker than usual.
81-88	$P_6A_8R_3D_3H_1$	89.3 (av. of 2 batches)	1.21	Ac_2O to 1st nitrator 3.3 g./min. high; to 2nd nitrator 1.1 g./min. low. Vessels were emptied and cleaned. The subsequent coating rate was slower than above.
89-106	$P_6A_8R_3D_3H_1$	91.2 (av. of 4 batches)	1.35	Ac_2O to 1st nitrator normal A_8; to 2nd nitrator 1.1 g./min. high. Coating bad in all vessels.
AVERAGE		86.6	1.29	

Note: The results are based on analysis of approximately each 4th batch. The remainder was not evaluated. The collection time was one hour per batch. Throughout the run excessive coating in all vessels was removed manually. Nitrators of Design I were used. During the 62 hours beginning with the 28th hour, the equipment was operated without a shut-down.

BIBLIOGRAPHY

1. Holston Defense Corporation report, "The Laboratory and Pilot Plant Preparation of HMX and 75-25 Octol", Control No. 20-T-14, 10 November 1952.

2. Holston Defense Corporation report, "The Laboratory and Pilot Plant Preparation of HMX and 75-25 Octol - Report No. II", Control No. 20-T-14A, 8 March 1953.

3. Holston Defense Corporation report, "The Laboratory and Pilot Plant Preparation of HMX and 75-25 Octol - Report No. III", Control No. 20-T-14B, 17 January 1955.

4. Samuel Feltman Ammunition Laboratories (Picatinny Arsenal) report, "An Improved Batch Process for the Preparation of HMX", Technical Report 2059, August 1954.

5. Holston Defense Corporation report, "Laboratory Continuous Incorporation of Composition B", Control No. 20-T-19, 13 May 1954.

6. Holston Defense Corporation report, "Spectrophotometric Determination of RDX", Control No. 20-T-17, 6 July 1953.

7. R. B. MacMullin and M. Weber, Jr., "The Theory of Short-Circuiting in Continuous Flow Mixing Vessels in Series and the Kinetics of Chemical Reactions in Such Systems", Trans. Am. Inst. Chem. Engrs., 31, 409-458 (1935).

8. Office of Scientific Research and Development report, "The Chemistry of Cyclonite", October 1, 1943, by G. C. Bassler.

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